13

THE DIELECTRIC PROPERTIES OF DIFFERENT MIXTURES OF HARD AND SOFT LAC RESIN

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ABSTRACT. The dielectric properties of mixtures of hard lac and soft lac have been measured over a wide range of frequency and temperature and the results analysed in the light of those obtained previous for whole lac as well as its constituents. The anomalous dielectric loss behaviour of whole lac compared to those of its constituents has been traced to the presence of a small amount of moisture which lac retains even on ordinary desiccation. It has been shown that this moisture is in the combined state and cannot be in the free state. The nature of this moisture, whether extraneous or not, has been fully discussed.

INTRODUCTION

In two previous papers of this series (Bhattacharya, 1944) it has been reported that both lac resin and its two chief constituents behave as typical polar resins in the a.c. field. But there is a slight difference in the behaviour of whole lac from that of either soft or hard lac regarding dielectric loss. In the case of whole lac the maximum value of dielectric loss slowly increases with the decrease of frequency whereas for either soft or hard lac this effect is not distinctly visible. In the case of these constituents ϵ_m'' the maximum value of loss is more or less constant throughout the range of frequency investigated. According to our present knowledge lac, as, such is simply a mixture of three main constituent bodies, *viz.*, (1) hard lac, pure lac or α-lac (2) soft lac and (3) lac wax. Of these three constituents the last one does not usually comprise more than 5% of the total lac and its loss has also been observed to be very small. The other two constituents are, therefore, mainly responsible for the loss of whole lac. Now the maximum value of dielectric loss at the lower frequencies for both hard and soft lac lies near about 0.5 whilst ϵ_m'' for whole lac is definitely more than this figure and is approximately 0.7 at 50 c/sec. It is difficult to explain this increased loss if it is supposed that lac is a solid solution of hard lac in soft lac. In order to see whether a mixture of dry hard and soft lac in the proportion in which they are present in whole lac also exhibits similar behaviour regarding loss, this investigation was undertaken. The plan was to take a few mixtures of desiccated hard lac and soft lac in different proportions, determine their dielectric properties and see if the results follow any general rule regarding dielectric loss and temperature shift for compositions containing different proportion of constituents. For it has already been observed that the presence of soft resin in lac is responsible for diminishing the internal viscosity of hard lac and so shifts the dielectric loss curve towards the low temperature side. In other words soft resin acts as a plasticiser for hard lac and whole lac is only a plasticised hard lac with soft lac so far as dielectric properties are concerned. Other workers (Fuoss, 1941 ; Davies, Miller and Busse, 1941) have also studied the effect of plasticiser content on some synthetic resins and found that an increase of plasticiser results in the decrease of internal viscosity of the resin and this is manifested by a shift towards the low temperature side of the loss curve.

THEORETICAL

We know that the complex dielectric constant ϵ of a substance in usually expressed as

$$\epsilon = \epsilon' - i\epsilon''$$

where ϵ' = the real or ordinary dielectric constant, and ϵ'' = the imaginary part or the loss factor ; and that $\epsilon'' = \epsilon' \tan \delta$, δ being the complementary phase angle or the loss angle. Thus both ϵ' and ϵ'' can be determined over any capacity bridge, which usually gives the value of capacity of a condenser and its power factor, tan δ.

But the expression for current in phase with the applied voltage is

$$I_r = I \tan \delta = \omega CV \tan \delta = 2\pi f CV \frac{\epsilon''}{\epsilon'} = \frac{fAV\epsilon''}{d \times 18 \times 10^{11}}$$

Since $C = \frac{A\epsilon'}{4\pi d \times 9 \times 10^{11}}$ farads for a parallel plate condenser

And if K_t is the total conductance of this condenser

$$I_r = \frac{AV.Kt}{d}$$

Hence from the last two equations, we have

$$\epsilon'' = \frac{18 \times 10^{11} \times Kt}{f}$$

A part of this loss will be due to d.c. conductivity of the material if that is appreciable and its measure will be

$$\epsilon''_{k_o} = \frac{10'' \times 18 \times Ko.}{f}$$

Hence pure a.c. loss is given by $\epsilon'' = \frac{18 \times 10^{11} \times (Kt\text{-}Ko)}{f} = \frac{18 \times 10^{11} \times K}{f}$

EXPERIMENTAL

Apparatus.—A Schering bridge was used for the determination of dielectric constant and power factor at lower frequencies and a General Radio radio-frequency bridge which is a modified form of Schering bridge was employed at higher frequencies. These bridges were the same as had been used on previous occasions.

Electrodes.—The vertical type parallel plate gold condenser which has already been described was utilised for different mixtures of soft and hard lac. The mixtures were taken in such proportions that they could be easily melted and the gold condenser put in that molten mass.

Materials.—The samples of soft and hard lac used for these experiments were the same as had been used for the determination of their dielectric properties. The details of the method of purification of these lac constituents have been reported in a previous paper (Bhattacharya, *loc. cit.*)

Method of procedure.—The required quantities of the two lac constituents were weighed separately according to the proportion taken and then they were mixed up intimately using the following method. This procedure was found most suitable after many attempts to mix them thoroughly and intimately were made. Soft lac was first taken in a basin and melted

TABLE II (*contd.*)

Frequency	Temp. °C	100% S. L. R.	80% S. L. R. 20% H. L. R.	50% S. L. R. 50% H. L. R.	30% S. L. R. 70% H. L. R.	100% H. L. R.
1 Kc/s	30°	0·282	0·122	0·046	0·024	0·028
	40°	0·465	0·241	0·109	0·043	0·005
	50°	0·400	0·411	0·232	0·100	0·100
	60°	0·259	0·463	0·408	0·231	0·091
	70°	0·128	0·252	0·486	0·490	0·400
	80°	—	0·098	0·281	0·482	0·540
	90°	—	—	0·099	0·263	0·410

DISCUSSION

The results have been shown in Tables I and II in which data for soft resin and pure lac resin have been taken from the previous paper of this series. Figures 1, 2, 3 and 4 show the dielectric constant-temperature relationship for these resin mixtures as well as soft resin and pure resin at 50 c/s, 1 Kc/s, 10 Kc/s and 100 Kc/s respectively. Figures 5 and 6 show their dielectric loss-temperature variation at 50 c/s and 1 Kc/s. All these curves belong to a group in which gradual transition from one to the other may be made by simply increasing or decreasing one or the other component. Thus from Figs 1, 2, 3, 4, 5 and 6 curve A representing 100% soft resin and curve E representing 100% pure resin there may be seen three curves B, C and D whose nature gradually changes from that of A to E. Figure 7 shows the variation of dielectric loss with the composition of the mixture of soft and hard lac resins at constant temperatures. The nature of these curves, it may be seen from the above figure, is similar to a dielectric loss temperature curve at constant frequency when a definite composition is taken. But there is a distinct difference which may be noted. At lower temperatures, such as 30°C or 40°C, these loss curves rise sharply to a peak and then fall again to low values. As the temperature gradually rises these peaks become more and more blunt

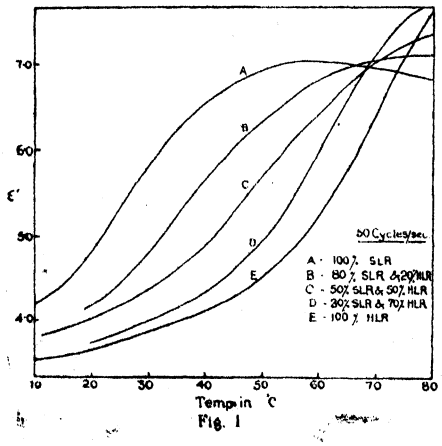

Fig. 1

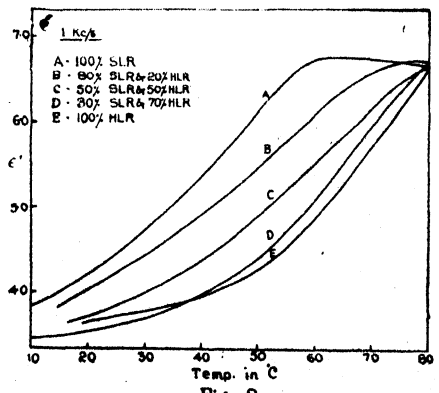

Fig. 2.

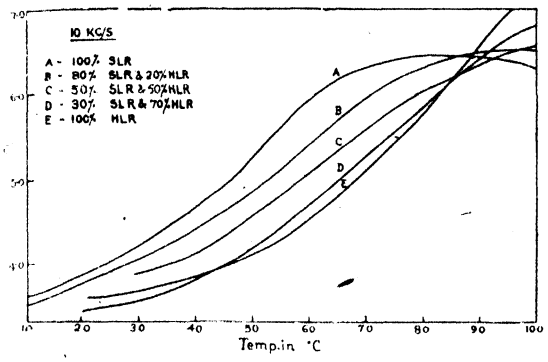

Fig.3

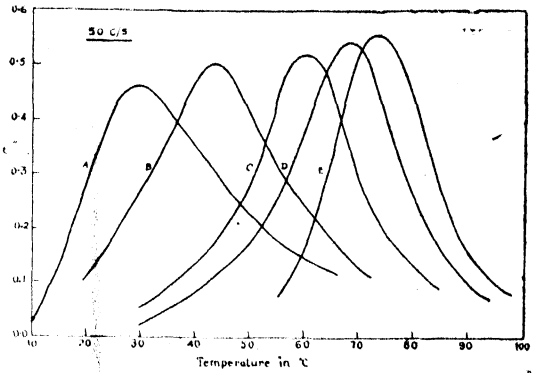

Fig.5.

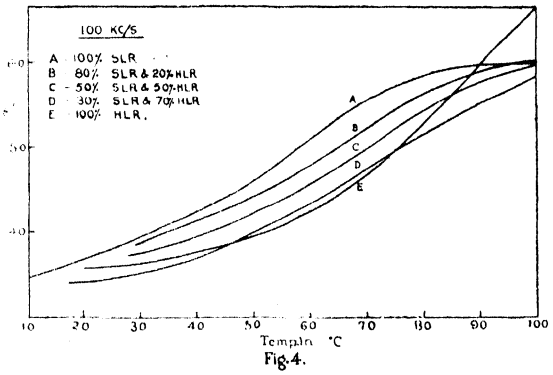

Fig.4.

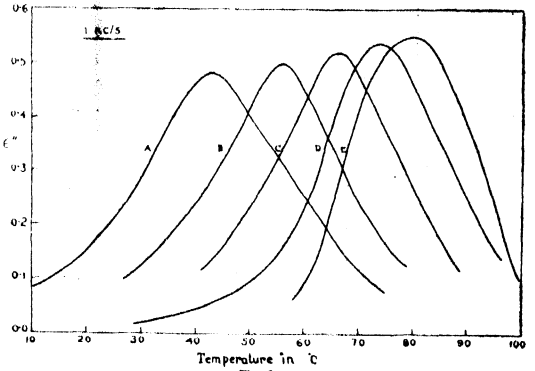

Fig.6.

till at about 70°C the peak becomes very blunt. The physical meaning of this bluntness is that near about such temperature the loss is insensitive to soft resin content of the mixture up to about (Fig. 7) 25-30%. In electrical machines usually a temprature rise of 40°C is permitted above the room temperature. In tropical countries, such as India, this means that the

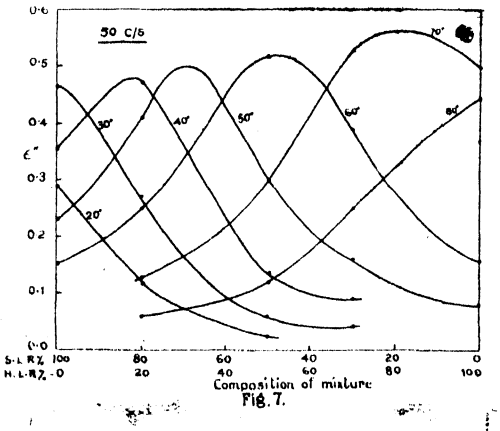

Fig.7.

machines may attain a temperature of 70°C. In such a case practically no advantage will be obtained by using pure lac resin instead of whole lac so far as loss is concerned. But if the temperature attained in the machine is only 60°C or slightly less definite advantage may be obtained by such use. If the temperature, however, falls below 50°C very little advantage may be gained since the value of loss becomes very low in both the cases.

TABLE III

Comparative dielectric constant and dielectric loss data of whole lac and a mixture of hard lac and soft lac of similar composition

Frequeney	Temp. °C	Whole lac (Kusmi)	Resin mixture	Difference	Whole lac (Kusmi)	Resin Mixture	Difference
50 c/s.	30°	3·91	3·96	−0·05	·020	·022	−0·002
	40°	4·28	4·30	−0·02	·051	·076	−0·025
	50°	4·95	4·90	0·05	·200	·180	0·020
	60°	6·00	6·00	0·00	·511	·371	0·140
	70°	7·12	7·10	0·02	·710	·535	0·178
	80°	7·85	7·80	0·05	·435	·261	0·174
1 Kc/s	30°	3·69	3·68	0·01	·026	·024	0·002
	40°	3·92	3·90	0·02	·039	·043	-0·004
	50°	4·36	4·34	0·02	·119	·100	0·019
	60°	5·08	5·06	0·02	·324	·231	0·093
	70°	5·96	5·95	0·01	·606	490	0·116
	80°	6·72	6·70	−0·02	·629	·482	0·147
	90°	7·36	7·35	0·01	·329	·263	0·066
10 Kc/s	30°	3·57	3·57	0·00	·044	·041	0·003
	40°	3·75	3·76	−0·01	·049	·045	0·004
	50°	4·18	4·16	0·02	·098	·101	−0·003
	60°	4·65	4·60	0·05	·203	·200	0·003
	70°	5·22	5·20	0·02	·383	·376	0·007
	80°	5·80	5·80	0·00	·512	·502	0·010
	90°	6.46	6·43	0·03	·537	·523	0·014
100 Kc/s	30°	3·48	3·46	0·02	·086	·084	0·002
	40°	3·67	3·66	0·01	·089	·088	0·001
	50°	4·00	4·01	−0·01	·112	·110	0·002
	60°	4·37	4·36	0·01	·157	·158	−0·001
	70°	4·76	4·77	−0·01	·256	·254	0·002
	80°	5·04	5·04	0·00	·357	·352	0·005
	90°	5·42	5·41	0·01	·443	·440	0·003

We shall now compare the curve D in Fig. 5 representing a mixture of 70% hard lac resin and 30% soft lac resin with that of Kusmi lac reported earlier. Table III shows these data for dielectric constant ϵ' as well as loss factor ϵ''. It may be seen that dielectric constant data at practically all frequencies agree quite well, but ϵ'' data differ, the difference in general diminishing with increasing frequency. Thus the difference between ϵ'' values of Kusmi lac and the corresponding values of resin mixture at any temperature for 100 Kc/s is practically negligible, for 10 Kc/s very slight, whereas for 1 Kc/s it is appreciable and for 50 c/s quite large. We have already pointed out that the maximum value of dielectric loss of pure lac resin for practically all frequencies is near about 0.55 and of soft resin 0.50, the temperature at which such maximum loss takes place depending upon frequency. For any composition of these constituent mixtures ϵ_m'' should lie within these limits provided no association takes place. In fact different compositions of mixture of these resins show that there is no abnormality present in their behaviour from that of their constituents, i.e, no association of any sort is taking place between their molecules.

The unexpected high value of ϵ_m'' of whole lac especially at lower frequencies seems at first sight very peculiar and even one may be tempted to doubt the proposition that lac is a simple mixture of soft and hard lac. But we have arrived at the above proposition from different angles of view (Bhattacharya, 1943) and the anomaly which exists in the behaviour of lac may be explained if it is supposed that a third substance is present in lac. This has actually been found to be moisture. In fact vacuum desiccation at an elevated temperature of 40°-45°C for 5-6 hours has been found to diminish this maximum loss considerably though not completely. It must be stated here that it is comparatively easier to free lac constituents from moisture than lac itself. This is probably due to the fact that pure lac resin becomes very crisp and porous during its preparation from lac and when in fine powder form it readily gives out its absorbed or adsorbed moisture, while soft resin itself does neither take up moisture so readily nor retain it so tenaciously. In lac, however, moisture, which is probably held by pure resin, is prevented from escaping easily by soft resin which serves as a coating. The difference in loss behaviour of the same sample of Kusmi lac after ordinary desiccation over calcium chloride overnight and after vacuum desiccation at 40°-45°C for about 6 hours has been shown

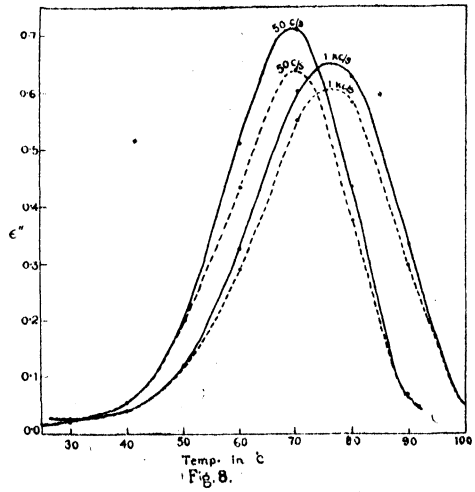

Fig. 8.

in figure 8 and the data included in Table IV. This clearly shows that the anomalous higher loss may be reduced by prolonged and efficient desiccation.

TABLE IV

Dielectric loss of whole lac (Kusmi) before and after vacuum desiccation at 40°-45°C. for 6 hours.

Frequency.	Temp. °C	After overnight desiccation over $CaCl_2$.	After vacuum desiccation at 40°-45°C.	Frequency.	After overnight desiccation over $CaCl_2$.	After vacuum desiccation at 40°-45°C.
50 c/s.	30°	·020	·022	1 Kc/s.	026	·024
	40°	·051	·050		039	·040
	50°	·200	·192		·119	·114
	60°	·511	·430		·324	·293
	70°	·710	·642		·606	·551
	80°	·435	·371		·629	·582
	90°	—	·070		·329	·296

It is not known how moisture is retained by lac. But it must be said that it is not present in the free state. In that case it would have contributed towards the increase of dielectric constant and not loss factor. For, at frequencies at which measurements were made water molecule should freely orient with the alternating field and should not show any anomalous dispersion at all. Hence its dielectric constant should have been high but loss negligible. It is seen however that such is not the case. The difference of dielectric constant values of Kusmi lac and the resin mixture is very small and of loss factor appreciable. Thus it can be explained only when this moisture is in a combined state. It is difficult to say how this moisture can be in the combined state and if absorbed or adsorbed moisture can behave in this fashion, but Langmuir and others (Adam. 1930$_a$) have shown that adsorbed gases are sometimes held by metal surfaces so tenaciously that it is difficult to distinguish between such an adsorbed state and a combined state. It is also known how extremely difficult it is to free a glass surface of its adsorbed gases including water vapour. Even prolonged heating near about the softening point of glass under high vacuum has been found to be ineffective in complely removing all adsorbed gases (Adam, 1930$_b$). It is, therefore, supposed that the phenomenon may not be confined to the surface only but probably the gases are absorbed some distance into the material. Langmuir (1918) has also found out that the amount of water vapour adsorbed by mica corresponds to two molecules thick, one layer of which probably forms part of the mica lattice structure. Thus we see that water vapour or more generally gases, adsorbed or absorbed by certain materials may be held so tenaciously that they behave as if in a combined state with those materials. It is, therefore, not unnatural to see that the absorbed water vapour in lac behaves in this fashion.

We can also look at the picture from another angle. This is to suppose that the moisture eliminated from lac at the elevated temperature of 40°-45°C under vacuum is actually not extraneous but results from slow condensation-polymerisation of lac. In such a case we shall have to take it for granted that during its preparation and desiccation under vacuum pure lac resin also gets considerably polymerised and hence its loss-maximum ϵ_m'', that we generally obtain by measurement on such a sample, is not the actual ϵ_m'' that we

could have expected had the sample not polymerised at all, but is a reduced figure owing to the elimination of some water. In such a case ϵ_m'' for all the resin mixtures, whose components are not polymerised, would have been higher and probably the value of ϵ_m'' of lac would have fitted in that series. The loss-temperature curve of Kusmi lac at any frequency could then reasonably belong to a group whose other members are obtained from mixtures of unpolymerised lac constituents at that frequency.

The latter explanation, though may seem at first sight unfamiliar, is not improbable or unreasonable, since lac is known to polymerise even at room temperature on ageing. It is probable, therefore, that lac polymerises much rapidly under vacuum at slightly higher temperatures. If we are prepared to accept this we shall have no hesitation in accepting also that pure lac resin under similar conditions will polymerise much more quickly. The usual method of drying lac or pure lac resin in a vacuum-oven at 40°C, therefore, may result in partial polymerisation. In the lac-trade of course this polymerisation or ageing is only tested by practical methods such as insolubility in cold or hot alcohol (Rangaswami and Sen, 1942), but there may be stages of this polymerisation in the early ones of which lac may be quite soluble even in cold alcohol. The cold alcohol solubility is, therefore, only a crude test of polymerisation and this is quite good from the consumers' point of view. But it is quite insensitive to the degree of polymerisation to which we are referring here, especially at the initial stages. Very recently such partially polymerised lac has been isolated from aged lac at this Institute (Sen, 1944) using mixed solvents and their molecular weight determination shows that they are higher than that of fresh lac. These partially polymerised lac are all soluble in cold alcohol. This fact, therefore, strengthens the latter explanation that pure lac resin usually gets partially polymerised during its preparation and drying and so the ϵ_m'' values obtained by measurement on such a sample are lower than what we should have obtained had the sample not polymerised at all.

It may, therefore, be concluded that moisture, whatever its nature may be, whether extraneous or not, is responsible for contributing to slightly higher loss to lac when compared to its constituents especially at lower frequencies. And this moisture is not present in the free state in lac but must be in the combined state. If it is extraneous moisture, we must explain this character by saying that the absorbed moisture forms part of the resin molecule by some sort of association. If, however, this moisture is not extraneous, it is expelled by a process of condensation—polymerisation of lac during vacuum desiccation.

ACKNOWLEDGMENT

The author expresses his indebtedness to Dr. H. K. Sen, Director of this Institute, for his kind interest in this work.

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